PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-060706

(43)Date of publication of application : 05.03.1999

(51)Int.Cl. C08G 63/199
C08G 63/193
G02B 1/04

(21)Application number : 09-218462

(22)Date of filing : 13.08.1997

(71)Applicant : OSAKA GAS CO LTD
SEIKO KAGAKU KOGYO CO LTD

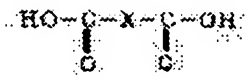
(72)Inventor : YAMADA MITSUAKI
MATSUYOSHI HIROAKI
SUDA YASUHIRO
YAMADA HIDETO
IWAIZUMI KUNIHIRO

(54) POLYESTER POLYMER AND ITS PRODUCTION

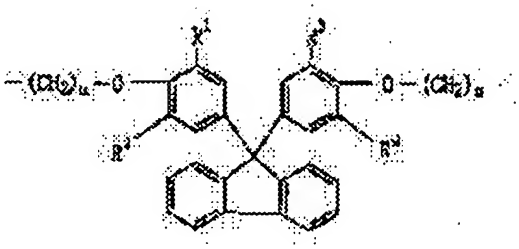
(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject polymer represented by a specific formula having high transparency, refractive index and heat resistance, small birefringence and water absorbability and suitable as a raw material for optical equipment.

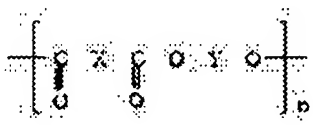
SOLUTION: A polyester polymer of formula III [X is an alicyclic hydrocarbon residue; X is a group of formula II; R1, R2, R3 and R4 are each H or a 1-4C alkyl; (m) is an integer of 2-4; (n) is an integer of ≥2]. The polymer of formula III is obtained by reacting an aliphatic dicarboxylic acid of formula I or its acid anhydride with a dihydroxy compound of formula II. The polymer of formula III preferably has a weight-average mol.wt. of ≥ 1000, and is useful as a raw material for optical lenses such as CD pickup lenses and Fresnel lenses, films such as projection television screens and phase difference films, plastic optical fibers and optical disk substrates.



I



II



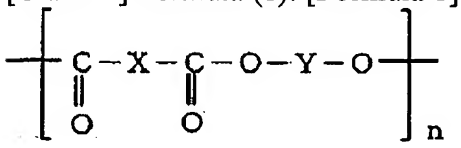
III

LEGAL STATUS

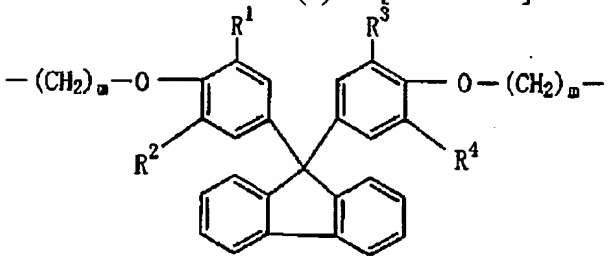
[Date of request for examination]	13.08.1997
[Date of sending the examiner's decision of rejection]	12.07.2000
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	
[Date of registration]	
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

CLAIMS

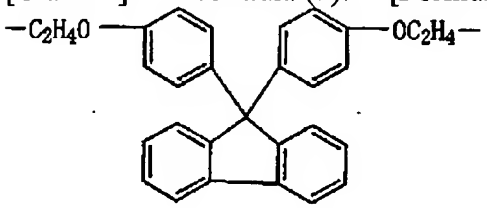
[Claim(s)]
[Claim 1] Formula (1): [Formula 1]



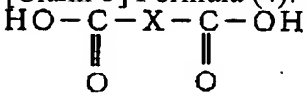
polyester polymer:X come out of and shown -- alicycle group hydrocarbon residue -- being shown -- Y -- formula (2): -- [Formula 2]



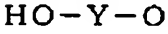
An example, and R1, R2, R3 and R4 show the alkyl group of H or carbon numbers 1-4 independently, m shows the integer of 2-4, and n shows two or more integers.
[Claim 2] The polyester polymer according to claim 1 whose X is 1 and 4-cyclo hexylene radical.
[Claim 3] Y -- formula (3): -- [Formula 3]



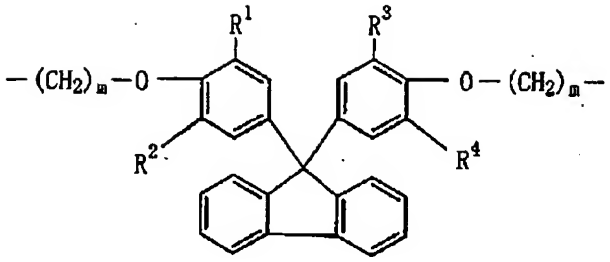
It comes out and is a certain polyester polymer according to claim 1.
[Claim 4] The poly ester polymer according to claim 1 whose weight average molecular weight is 1000 or more.
[Claim 5] Formula (4): [Formula 4]



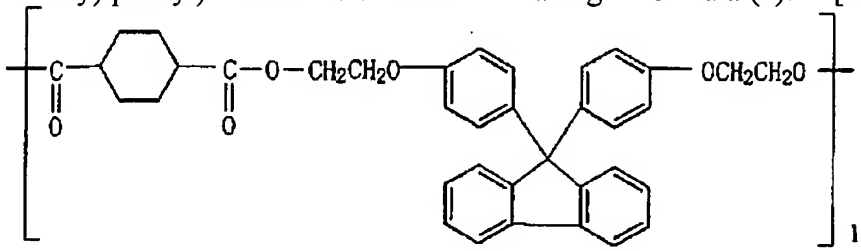
The alicycle group dicarboxylic acid come out of and shown or its acid anhydride, and a formula (5): [Formula 5]



manufacture approach:X of the poly ester polymer characterized by coming out, making the dihydroxy compound shown react, and obtaining a polyester polymer according to claim 1 -- alicycle group hydrocarbon residue -- being shown -- Y -- formula (2): -- [Formula 6]



An example, and R1, R2, R3 and R4 show the alkyl group of H or carbon numbers 1-4 independently, and m shows the integer of 2-4.
[Claim 6] 1 and 4-cyclohexane dicarboxylic acid and a 9 and 9-bis(4-(2-hydroxy ethoxy) phenyl) fluorene are reacted -- making -- formula (6): -- [Formula 7]



Manufacture approach:, however l of the polyester polymer characterized by coming out and obtaining the polyester polymer shown show two or more integers.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to a polyester polymer suitable as a detailed raw material for optical instruments with small rate of a birefringence and absorptivity with high and transparency, a refractive index, and thermal resistance about the polyester which has a fluorene frame. The polyester polymer of this invention is useful as a raw material of CD pickup lens, an optical lens like a Fresnel lens, the screen for projection TV, a film like a phase contrast film, a plastic optical fiber, and an optical disk substrate.
[0002]
[Description of the Prior Art] There is polymethylmethacrylate (PMMA) as most typical plastic material for optics. PMMA has transparency and weatherability, and since the rate of a birefringence is small and a moldability is also good, it is used for CD pickup lens, an optical lens like a Fresnel lens, the screen for projection TV, a film like a phase contrast film, the plastic optical fiber, the optical disk substrate, etc. However, it is inadequate absorptivity and in respect of thermal resistance. Since especially absorptivity is high, in using it for a lens, there is a fault that profile irregularity collapses by the environmental variation, or a refractive index changes and the aberration of a lens increases. Moreover, in using it for an optical

disk substrate, expansion, deformation, and curvature are produced by water absorption, and it causes the increment in an error.

[0003] The polycarbonate (PC) serves as an ingredient important as an optical material subsequently from transparency, thermal resistance, shock resistance, low absorptivity, etc. at PMMA. However, there is a fault that the most important rate of a birefringence in an optical property is high. If the rate of a birefringence is large, when using it for an optical disk, the polarization direction of the reflected light shifts, the light which reaches a detecting element decreases, and it becomes the cause which a noise increases.

[0004] The new polymer of an amorphous annular polyolefine system is developed as an optical material which improved absorptivity and the rate of a birefringence. That is, the polymerization of ethylene, the copolymer of an annular olefin, and the polycyclic norbornene system monomer is carried out, and there are hydrogenated amorphous polyolefine, a polycyclic norbornene system methacrylate copolymer, etc. However, although absorptivity and the rate of a birefringence are the optical materials excellent very small, as for each of these, no refractive indexes exceed 1.60.

[0005]

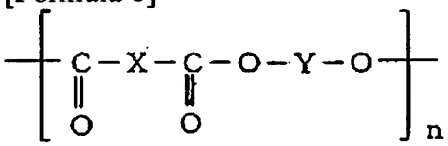
[Problem(s) to be Solved by the Invention] This invention aims concrete at offering a polyester polymer with low rate of a birefringence and absorptivity with a high and refractive index for the purpose of offering a polyester polymer useful as an optical material.

[0006]

[Means for Solving the Problem] The polyester polymer using a specific monomer is a high refractive index, and is a rate of a low birefringence, and this invention persons came to complete a header and this invention for excelling also in absorptivity, as a result of repeating examination wholeheartedly in view of the trouble of the above-mentioned conventional technique.

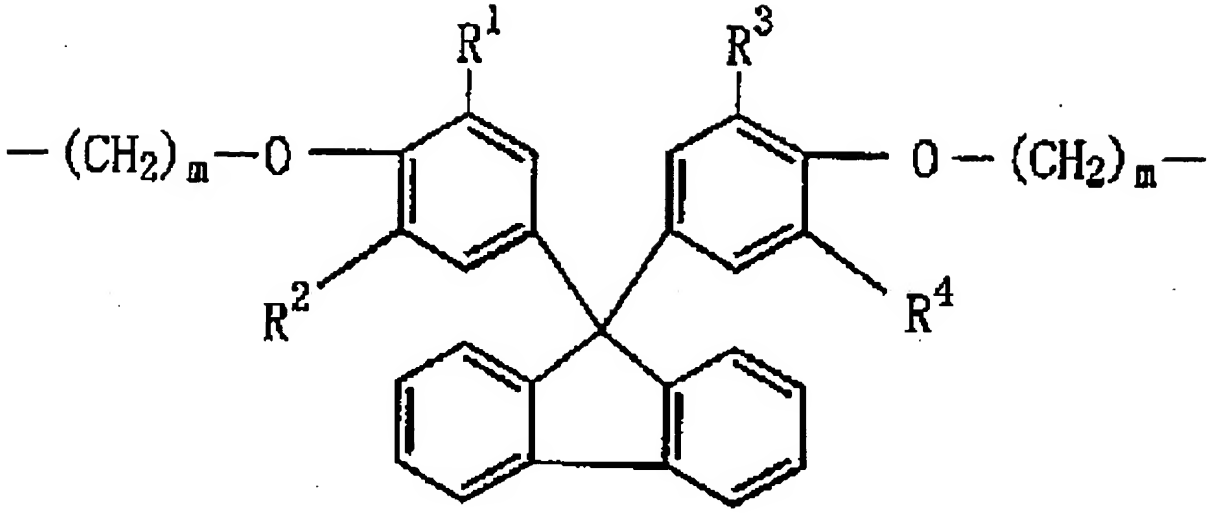
[0007] That is, this invention is :1. which is a thing concerning a following polyester polymer and its following manufacture approach. Formula (1) : [0008]

[Formula 8]



[0009] It comes out, polyester polymer:X shown shows alicycle group hydrocarbon residue, and Y is formula (2): [0010].

[Formula 9]

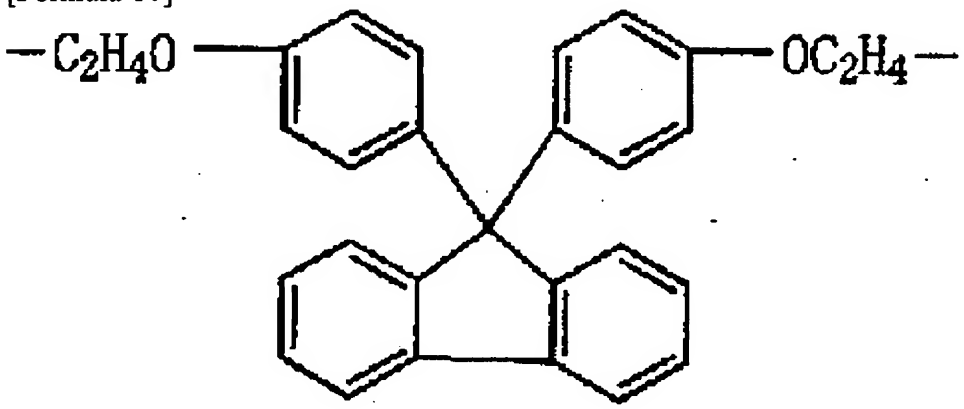


[0011] An example, and R1, R2, R3 and R4 show the alkyl group of H or carbon numbers 1-4 independently, m shows the integer of 2-4, and n shows two or more integers.

[0012] 2. Polyester polymer given in said term 1 whose X is 1 and 4-cyclo hexylene radical.

[0013] 3. Y is Formula (3): [0014].

[Formula 10]

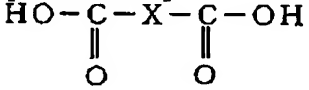


[0015] It comes out and is a polyester polymer given in said a certain term 1.

[0016] 4. Poly ester polymer given in said term 1 whose weight average molecular weight is 1000 or more.

[0017] 5. Formula (4) : [0018]

[Formula 11]



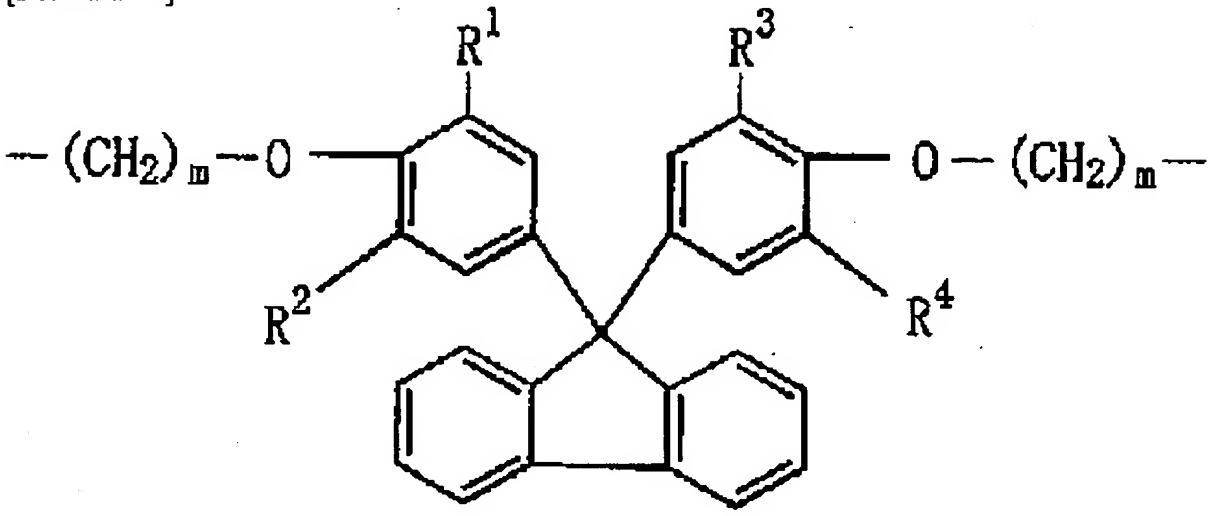
[0019] The alicycle group dicarboxylic acid come out of and shown or its acid anhydride, and formula (5) : [0020]

[Formula 12]

$$HO-Y-OH$$

[0021] Manufacture approach:X of the poly ester polymer characterized by coming out, making the dihydroxy compound shown react, and obtaining the polyester polymer of a publication in said term 1 shows alicycle group hydrocarbon residue, and Y is formula (2): [0022].

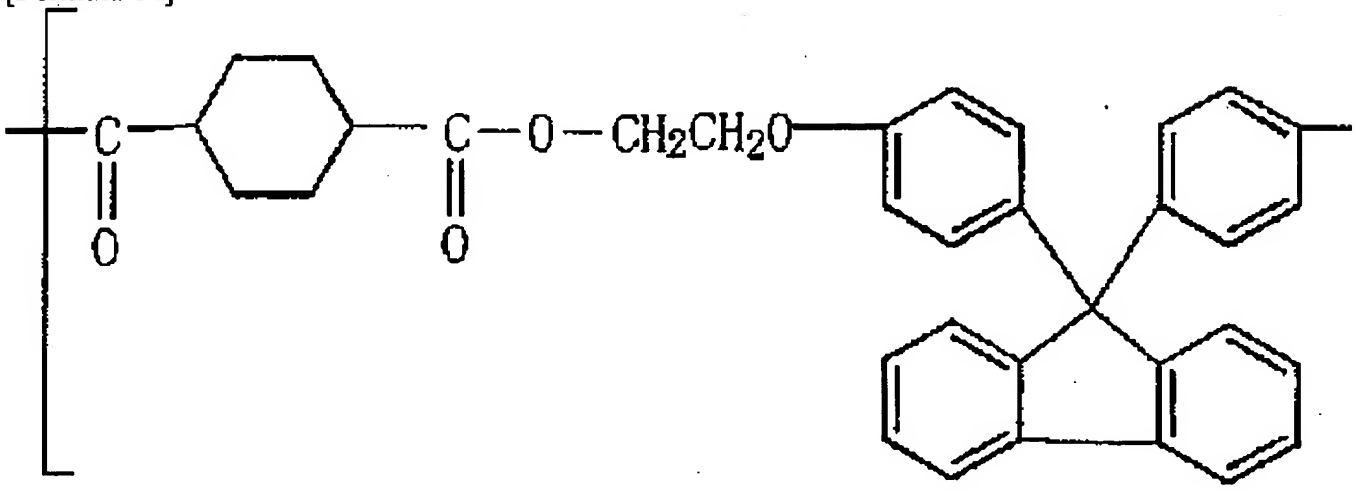
[Formula 13]



[0023] An example, and R1, R2, R3 and R4 show the alkyl group of H or carbon numbers 1-4 independently, and m shows the integer of 2-4.

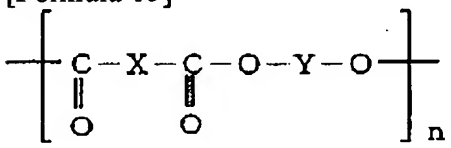
[0024] 6. Make 1 and 4-Cyclohexane Dicarboxylic Acid and 9 and 9-Bis(4-(2-Hydroxy Ethoxy) Phenyl) Fluorene React, and it is Formula (6): [0025].

[Formula 14]



[0026] Manufacture approach:, however l of the poly ester polymer characterized by coming out and obtaining the polyester polymer shown show two or more integers.

[0027]
[Embodiment of the Invention] Hereafter, this invention is explained with the gestalt of the operation.
[0028] The polyester polymer of polyester polymer this invention has the structure which the alicycle group dicarboxylic acid of a formula (4) or its acid anhydride, and the dihydroxy compound of a formula (5) are made to react, and is acquired. The polyester polymer of this invention is formula (1): [0029].
[Formula 15]



[0030] It comes out and has the structure shown. n shows the polymerization degree of a repeating unit among a formula (1), and two or more integers and usual show the integer of 5-100.
[0031] The flat surface of a fluorene ring and its flat surface of the benzene ring are very effective as a monomer which gives the effectiveness of reducing the rate of a birefringence resulting from the conformation which intersects perpendicularly mutually while the dihydroxy compound of a formula (5) raises the thermal resistance of a polyester polymer, and a refractive index by having an upright fluorene ring and the 2 benzene rings.
[0032] Although the thermal resistance of a polyester polymer and a refractive index improve by the aromatic series ring (benzene ring) when using aromatic series dicarboxylic acid, such as a terephthalic acid, as a dicarboxylic acid component, the rate of a birefringence becomes large. In order that the Abbe number showing a distributed property may decrease with lifting of a refractive index, installation of the aromatic series ring by aromatic series dicarboxylic acid must be performed in consideration of the balance of a refractive index and the Abbe number. In this invention, the increment in the rate of a birefringence and lowering of the Abbe number can be controlled, without reducing thermal resistance by using the alicycle group dicarboxylic acid of a formula (4).
[0033] Although the bis-phenyl fluorene radical and the alkylene glycol residue of a hydrophilic property which may have a hydrophobic alkyl group in dihydroxy compound residue (Y) live together, the molecular weight of the bis-phenyl fluorene residue which may have an alkyl group is large (a content is), and since the polyester polymer of this invention has few contents of ethylene glycol residue, it is considered that water absorption becomes low.
[0034] Generally, if the limiting viscosity of a polymer is high, the fluidity at the time of shaping will worsen, will produce the stress-strain diagram and molecular orientation of mold goods, and will cause lifting of the rate of a birefringence. In the polycarbonate, by lowering molecular weight, limiting viscosity is made low and lifting of the rate of a birefringence is eased. In this invention, it is easing that the fluidity at the time of polyester polymer shaping worsens by using not aromatic series dicarboxylic acid but the alicycle group dicarboxylic acid which has the structure which hydrogenated [perfect-] or hydrogenated [partial-] the aromatic series ring of aromatic series dicarboxylic acid as a dicarboxylic acid component.

[0035] the weight average molecular weight into which the polyester polymer of this invention converted polystyrene as a criterion using gel permeation chromatography -- 1000 or more -- desirable -- 1000-50000 -- it is 5000-40000 still more preferably. If mechanical strength with weight average molecular weight sufficient by less than 1000 is not obtained but 50000 is exceeded, the fluidity at the time of shaping will be bad, and the rate of a birefringence of mold goods will worsen.

[0036] The polyester polymer of manufacture approach this invention of a polyester polymer can be manufactured by making the alicycle group dicarboxylic acid of a formula (4) or its acid anhydride, and the dihydroxy compound of a formula (5) react.

[0037] As the alicycle group dicarboxylic acid of a formula (4), or its acid anhydride, well-known alicycle group dicarboxylic acid or its anhydride can be used. As alicycle group dicarboxylic acid, alicycle group dicarboxylic acid, such as 1, 4-cyclohexane dicarboxylic acid (CHDA), 1, 3-cyclohexane dicarboxylic acid, 1, 2-cyclohexane dicarboxylic acid, tetrahydro phthalic anhydride, and hexahydro phthalic anhydride, or the acid anhydride of those can be used, for example.

[0038] as the dihydroxy compound of a formula (5) -- a 9 and 9-bis(4-(2-hydroxy ethoxy) phenyl) fluorene (BPEF), 9, and 9-bis(3-methyl-4-(2-hydroxy ethoxy) phenyl) fluorene, 9, and 9-bis(4-(2-hydroxy propoxy) phenyl) fluorene -- BPEF can be used preferably. As a dihydroxy compound, purity can use 98% or more of thing for what has high purity, and a concrete target preferably 95% or more.

[0039] the dihydroxy compound of a formula (5) -- for example, a hydroxy ethoxy benzene derivative and full -- me -- it can manufacture by carrying out the dehydration condensation reaction of the non. a hydroxy ethoxy benzene derivative and full -- me -- the mixed catalyst of an acid (for example, sulfuric acid) and a thiol can be used for the dehydration condensation reaction, non. For example, the manufacture approach of BPEF is indicated by the patent No. 2559332 official report (H8.9.5).

[0040] The ester polymerization reaction of the alicycle group dicarboxylic acid of a formula (4) and the dihydroxy compound of a formula (5) can be carried out by approaches, such as solvent polymerization methods, such as a well-known ester polymerization method, for example, an ester interchange method, and a direct polymerization method, a solution polymerization method, and interfacial polymerization. With the gestalt of desirable operation, the polyester polymer of this invention is manufactured by carrying out the esterification reaction of the alicycle group dicarboxylic acid of a formula (4), and the dihydroxy compound of a formula (5) by the direct polymerization method.

[0041] That a direct polymerization method does not have **** of alcohol like an ester interchange method, it can carry out, without needing a catalyst, and dicarboxylic acid cheaper than dicarboxylic acid diester can be used for a raw material etc. has many points [dominance / method / ester interchange]. In the usual polyester manufacture, an ester interchange method is used in many cases. the solubility of the dicarboxylic acid and the glycol (dihydroxy compound) which generally use this for the conventional polyester manufacture -- bad -- a direct polymerization method -- if -- it is because a reaction cannot advance easily.

[0042] However, when this invention persons found out, and the alicycle group dicarboxylic acid of a formula (4) or its acid anhydride (for example, CHDA), and the dihydroxy compound (for example, BPEF) of a formula (5) have high solubility, for example, use equimolar mixture as raw materials, an esterification reaction fully advances also on very mild conditions. According to this invention, 200-300 degrees C of the poly ester polymers of this invention can be manufactured by reacting at the temperature of 210-280 degrees C preferably under reduced pressure of 1 - 30torr extent under existence of a catalyst or nonexistence (when using the equimolar mixture of CHDA and BPEF as a raw material).
[0043] The esterification reaction of the alicycle group dicarboxylic acid of a formula (4) or its acid anhydride, and the dihydroxy compound of a formula (5) can be carried out without using a catalyst. Generally, a polyester polymer with more high polymerization degree can be manufactured by carrying out an esterification reaction more at an elevated temperature for a long time. However, if long duration operation of the esterification reaction is carried out at an elevated temperature, coloring of the polyester polymer obtained may be caused. On the other hand, by using a catalyst, polymerization degree predetermined on milder conditions can be acquired, and coloring of a polyester polymer can be prevented. As a catalyst, the metallic compounds of well-known antimony, a lithium, germanium, tin, titanium, zinc, aluminum, magnesium, calcium, manganese, and cobalt can be used.
[0044]
[Effect of the Invention] According to this invention, it has the outstanding optical property (transparency, high refractive index), thermal resistance, and absorptivity, and a polyester polymer useful as plastics for optics can be offered. The polyester polymer of this invention is useful as a raw material of CD pickup lens, an optical lens like a Fresnel lens, the screen for projection TV, a film like a phase contrast film, a plastic optical fiber, and an optical disk substrate, and can be widely used for an optical application. Since the manufacture approach of the polyester polymer of this invention is not based on an ester interchange method since it is based on a direct polymerization method namely, its economic effects are large.
[0045]
[Example]
[Manufacture of a polyester polymer]
Di-n-butyl tin oxide 0.305g was taught to two liter flasks as a catalyst at the example 1CHDA172g (1.0 mols) and BPEF438g (1.0 mols) list, and the esterification reaction was performed at 10 - 30mmHg and the temperature of 217 degrees C for 12 hours.
[0046] The esterification reaction was performed at the temperature of 237 degrees C for 6 hours, having taught di-n-butyl tin oxide 0.61g as a catalyst to two liter flasks at the example 2CHDA172g (1.0 mols) and BPEF438g (1.0 mols) list, fusing, carrying out reduced pressure deaeration by 10 - 30mmHg, and holding reduced pressure.
[0047] The temperature of 218-231 degrees C performed the esterification reaction with the non-catalyst for 12 hours, having taught example 3CHDA172g (1.0 mols) and BPEF482g (1.1 mols) to two liter flasks, fusing, carrying out reduced pressure deaeration by 10 - 30mmHg, and holding reduced pressure.

[0048] The esterification reaction was performed at the temperature of 271 degrees C for 5 hours, having taught di-n-butyl tin oxide 0.61g as a catalyst to two liter flasks at the example 4CHDA172g (1.0 mols) and BPEF438g (1.0 mols) list, fusing, carrying out reduced pressure deaeration by 10 - 30mmHg, and holding reduced pressure.
[0049] Di-n-butyl tin oxide 0.60g was taught to two liter flasks as a catalyst, and the esterification reaction was performed in 166g (1.0 mols) of example of comparison 1 terephthalic acids, and a BPEF438g (1.0 mols) list on the same conditions as an example 4 for 5 hours. The unreacted object of a terephthalic acid remained and what was distributed as a white grain in the polymer was obtained.
[0050] [Assessment of a polyester polymer] The following physical properties were measured about the polyester polymer of this invention manufactured according to each example. A result is shown in a table 1. The glass transition temperature, the rate of a birefringence, and water absorption which were measured about the commercial polycarbonate resin for optical disks (weight average molecular weight 17600, Tg123 degree C) are shown as an example 2 of a comparison.
[0051] (1) Molecular weight : gel permeation chromatography (HLC[by TOSOH CORP.]-8120GPC) was used, and it measured to the solvent using the tetrahydrofuran. A molecular-weight value is expressed as a standard reduced property for polystyrene.
[0052] (2) Glass transition temperature : it measured by part for programming-rate/of 10 degrees C using the differential scanning calorimeter (TAS[by the physical science electrical-and-electric-equipment company]- 100).
[0053] (3) Refractive index : diiodomethane was measured as contact liquid by the sodium D line with a wavelength of 589.3nm with Abbe refractometer Made from ATAGO.
[0054] (4) The rate of a birefringence : the 30mmx10mmx100micrometer film was used and it measured with the photoelasticity measuring device (PA[by Riken Keiki Co., Ltd.]- 150).
[0055] (5) Water absorption : the circular test piece with a diameter [of 50mm] and a thickness of 3mm was created, and it asked according to JIS-K7209 from the original weight of a test piece, and the ratio of the mass increment before and behind water absorption.
[0056]
[A table 1]
Weighted mean Tg Refractive index Rate of a birefringence Water absorption Acid number Molecular weight ** cm2/dyne % Example 1 10100 123 1.65 29x10-13 0.06 2.6 examples 2 27000 132 1.64 30x10-13 0.05 2.5 examples 3 8300 121 1.64 33x10-13 0.07 2.8 examples 4 37500 135 1.65 33x10-13 Example 1 of 0.062.6 comparisons 15200 149 - - - Example 217600 of 12.2 comparisons 123 1.59 65x10-13 0.11 [0057] As compared with the commercial polycarbonate resin for optics, the polyester polymer of a refractive index of this invention is expensive, and is plastics for optics which the rate of a birefringence and water absorption have sufficient thermal resistance, and was excellent in them low so that more clearly than a table 1. It is not necessary to measure, and is inferior to the unreacted object remaining considerably in respect of a refractive index and water absorption, and

the example 1 of a comparison is considered not to bear practical use.

[Translation done.]